Properties of the self-deforming N_{tb} phase in mesogenic dimers.

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ABSTRACT

An overview of the results obtained from the most recent experiments performed for revealing the structure of the twist-bend nematic N_{tb} phase will be presented at the conference. This new phase provides typical X-ray diffraction pattern for the nematic phase and is found at temperatures below the conventional nematic phase in odd-chain hydrocarbon linked mesogenic dimers. The materials in the N_{tb} phase form self-deformed striped pattern parallel to the rubbing direction in planarly aligned rubbed cells with a well-defined period. The period is found to depend on the cell spacing. The self-deformation stripes appear without any external electromagnetic field or thickness gradient across the cell. Although the materials are composed of non-chiral molecules, the low temperature nematic phase exhibits fast linear optical response of the order of a few microseconds. This response is reminiscent of the phase exhibiting chirality. Moreover, at higher fields some of the materials form striped domains with opposite direction of the optical response. These stripes appear normal to the rubbing direction and their periodicity depends on voltage and frequency. The Freedericksz transition in this phase also shows unusual properties and this is proven to be of the first order. The techniques to characterize this phase include polarized microscopy observation and optical contrast spectroscopy. Possible causes of the phenomena will be discussed.

Keywords: Dimers, self-deformation, striped pattern, optical response, N_{tb} phase, periodic domains, first order Freedericksz transition, nematic liquid crystals

1. INTRODUCTION

Molecules of mesogenic dimers are made by linking two rather usual mesogenic cores with a flexible hydrocarbon chain. In the case of an odd number of carbon atoms in the chain, the materials exhibit an additional phase which recently has attracted significant attention. The X-ray diffraction pattern corresponded to a typical nematic phase, although it shows clearly different behavior in most of the other experiments[1,2,3,4,5]. The phase was referred as the N_x in earlier works assuming the details of the molecular structure to be unknown. Meanwhile the most recent works[6,7] provide rather clear evidence of the presence of a nano-scale structure similar to the one predicted by R.B. Meyer[8] and I. Dozov[9]. However, a number of micro-scale properties need to be explained. In this paper we shall present the overview of overview some of the recently observed properties and give the data not included in the previously published manuscripts.

1.1 Liquid Crystalline Materials.

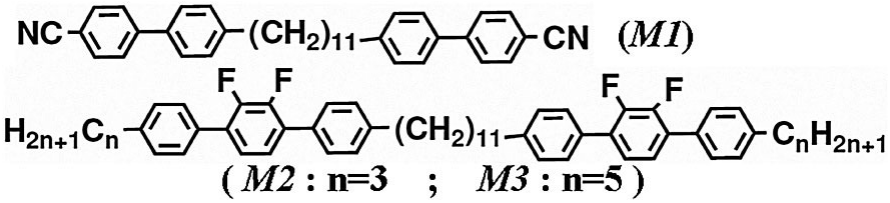

Figure 1. Liquid crystalline materials used. M1: Cr (91 °C) N_{tb} (109 °C) N (127 °C) Iso; M2: Cr (95 °C) N_{tb} (137 °C) N (193 °C) Iso; M3: Cr (85 °C) N_{tb} (123 °C) N (170 °C) Iso.

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The chemical structures of the materials used in our experiments are shown in Figure 1. They can have either positive (M1) or negative (M2, M3) dielectric anisotropy, this does not affect the nature of the N_{tb} phase. Moreover, the phase is still present when the dimers are mixed with other nematic materials such as 4-4'-pentyl-cyano-biphenyl (5CB) or the monomer of M3. This opens up an opportunity to tailor make the operating temperatures over a relatively wide range including the room temperature.

2. EXPERIMENTAL FINDINGS

2.1 Textures observed in planar cells.

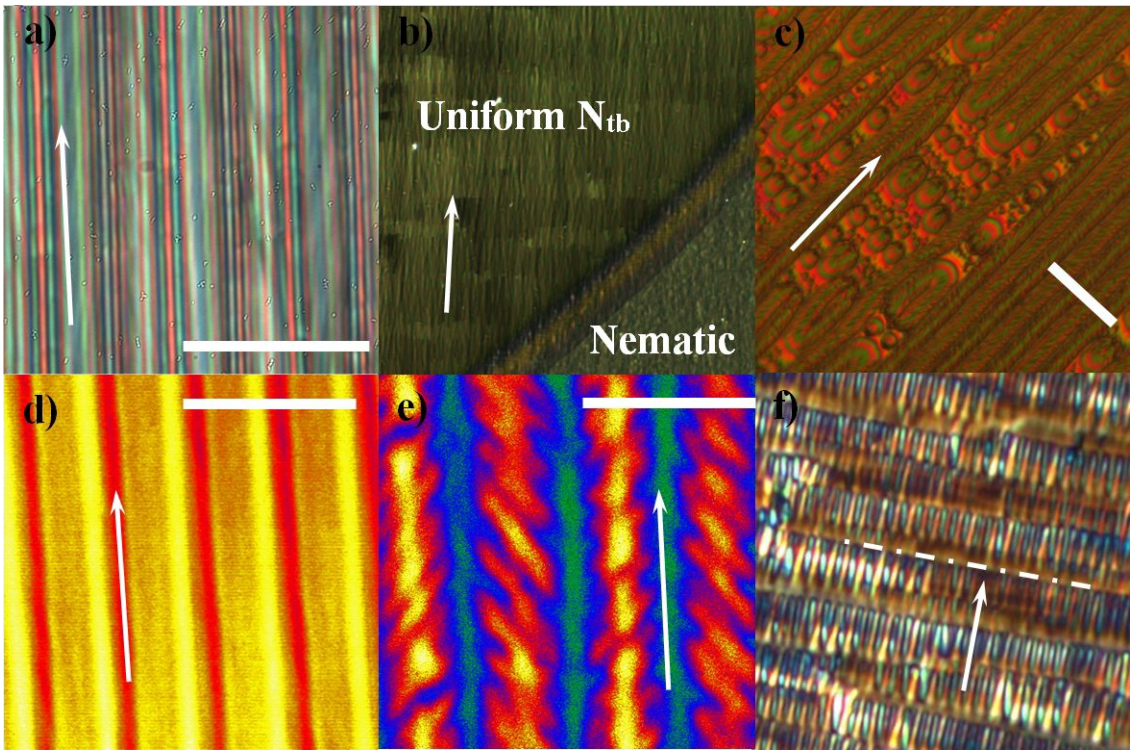

Figure 2. White arrows denote the rubbing direction. Crossed polarizers are parallel to the image frame. a) Planar cell, stripes in the N_{tb} phase, cell gap 15μm, white bar length - 30 μm; b) phase transition in planar cell, cell gap 8 μm; c) focal-conic domains in a 13μm thick cell, white bar length - 55μm; d), e) Fluorescent confocal polarizing microscopy (FCPM) image of 6 μm cell with and without super-texture, white bar length - 12 μm; f) hybrid cell, dash-dot line denotes a boundary between domains.

One of the first phenomena which attracted attention to the N_{tb} phase was the spontaneous appearance of the self-deformation pattern in planar cells. The periodicity of the pattern was defined by the cell geometry and in planar cells was equal to the double cell gap. The colors of the pattern indicate the deviation of the optical axis from both cell plane and the rubbing direction[1]. Figure 2 shows a series of patterns found under different boundary conditions. One must note that while the self-deformation pattern consisting of the periodic stripes parallel to the average molecular director (Figure 2a) is one of the main and the most stable characteristic features used to identify the N_{tb} phase, it does not necessarily appear in the entire range of the N_{tb} phase. In the cells with parallel rubbing on both surfaces the self-deformation pattern appears a few degrees below the transition temperature between the conventional nematic and the N_{tb} phase. The latter needs to be identified by less obvious features such as disappearance of the visible director fluctuations (Figure 2b). Apart from the stripes, thicker cells (thickness greater than 5-7 μm) also possess focal-conic pattern (Figure 2c). This observation may lead to a misidentification of the phase being smectic, although the layers responsible for formation of such domains in the N_{tb} phase are of different nature. The appearanve of the striped and focal-conic patterns is likely to be determined by a delicate interplay among surface conditions, material constants, thermal and electric field history of

the sample. The striped and focal conic patterns often co-exist. Moreover, the history of the sample apparently determines the existence of the fine super-texture reported for the striped patterns earlier[4]. Although sub-micron feature size of the super-texture does not allow for solid conclusions based on optical observations, more sophisticated techniques, such as the Fluorescent Confocal Polarizing Microscopy (FCPM) are able to reveal valuable information. Figures 2d and 2e show the FCPM images of the same sample taken at different times. One can clearly see that the super texture may or may not be present in the same cell depending on the temperature history and the ageing of the sample. This is a possible direction for further studies.

The surface conditions have dramatic effect on the pattern. Figure 2f shows the self-deformation pattern in a hybrid cell with one glass treated for homeotropic alignment and the other – for planar. One can see the self-deformation pattern "fine cut" by domain walls normal to the rubbing direction. The domains resemble those reported recently for the case of strong electric fields[3], thus a possible cause can be related to the surface polarization difference between the two surfaces typical for hybrid cells[10].

2.2 Experimental set-up.

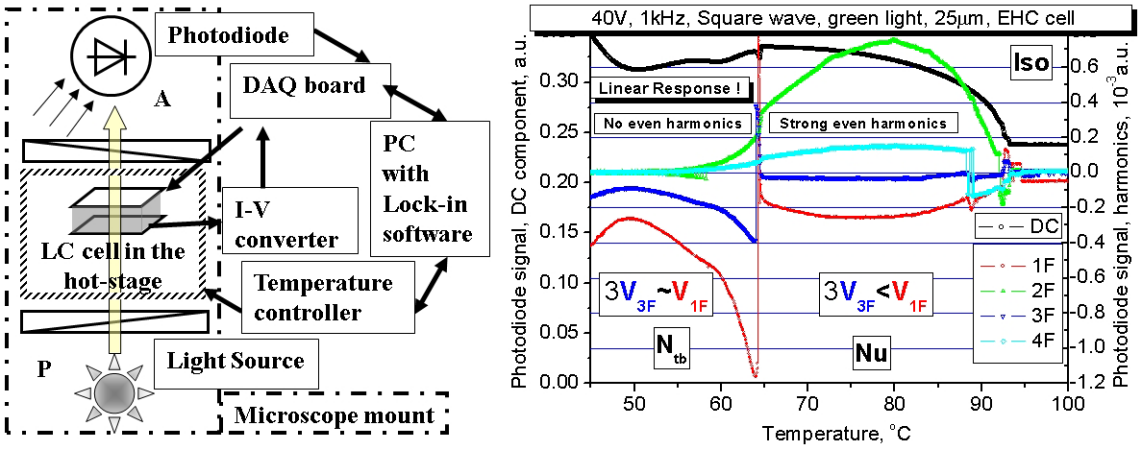

Figure3. Left: the optical contrast spectroscopy set-up. Right: Temperature dependence of the various harmonics of the optical response.

The set-up for investigation of the electro-optical properties of liquid crystals (Figure 3, left) includes a polarizing microscope with crossed polarizers, photodiode detector, oscilloscope, and/or lock-in amplifiers. The rubbing direction of a cell is set at 22.5° from the POM polarizer direction, the electric field with a square or sinusoidal waveform is applied to the cell from a multifunctional data acquisition board (National Instruments® NI-USB-6216) and the optical transmittance of the system is measured by a photodiode connected to an I-V converter and the data acquisition board. Our lock-in algorithm allows simultaneous extraction of the DC component and the first four harmonics of the photodiode current. Due to the narrow-band measurements, this optical contrast spectroscopy technique[11] detects the switching properties not visible by conventional oscilloscope or visual observation.

In the case of a linear (polar) response, the even harmonics must be zero while the first (fundamental) harmonic must present. If the response is linear and its switching time is much less than the period of the applied wave, the amplitude ratio between the first and the third harmonics should remain the same as in the applied square wave (i.e. $3V_{3F}=V_{1F}$). Alternatively, when the material does not show fast enough response (and, therefore, behaves as a low-pass filter) the level of the higher harmonics must be less than in the original waveform (i.e. for the square wave $3V_{3F}<V_{1F}$). Non-linear response (like quadratic response of the Nu phase) will generate even harmonics.

2.3 Microsecond optical response.

The right part of the Figure 3 demonstrates clear difference in behaviour between the N and N_{tb} phases.

The conventional nematic phase demonstrates a high-frequency residue of its normal (quadratic) behaviour and has clear low-pass filtering properties, while the response of the N_{tb} phase meets the above odd harmonic criteria for the fast polar

switching in the whole temperature range[3]. The odd harmonic signals had been detected in all the above materials and mixtures in cells with at least one planarly aligning surface.

The appearance of the striped spontaneous periodic deformations[1] at lower temperatures in the N_{tb} phase does not show conclusive influence on the observed switching, although all the optical transmittance signals are modified by the presence of this pattern. Moreover, the striped pattern vanishes at rather moderate fields for both positive and negative dielectric anisotropy materials while the described response remains.

For the materials with positive dielectric anisotropy the signals degrade rapidly when the applied voltage causes Freedericksz transition to a homeotropic state. The materials with negative dielectric anisotropy show this fast and linear response up to the breakdown voltages and the switching can be more easily observed by the other methods[3]. Linear response and the switching time of the order of 5 μs are found in the N_{tb} phase. Although the amplitude of the response correspond to the deviation of the optical axis ofone or two degrees when the voltages close to the breakdown are applied. This response resembles electroclinic effect or uniformly lying helix (ULH) switching. These two effects were originally attributed to the chiral materials, while all the molecules used in our experiments are non-chiral. However, recent NMR studies[12,13] shows the presence of chirality in the Ntb phase. It is suggested to be a consequence of the molecules having, on average, a bent structure, and the chirality of the phase then produces a small chiral biasing of the conformer distribution[13].

2.4 Field-induced periodic chiral domains.

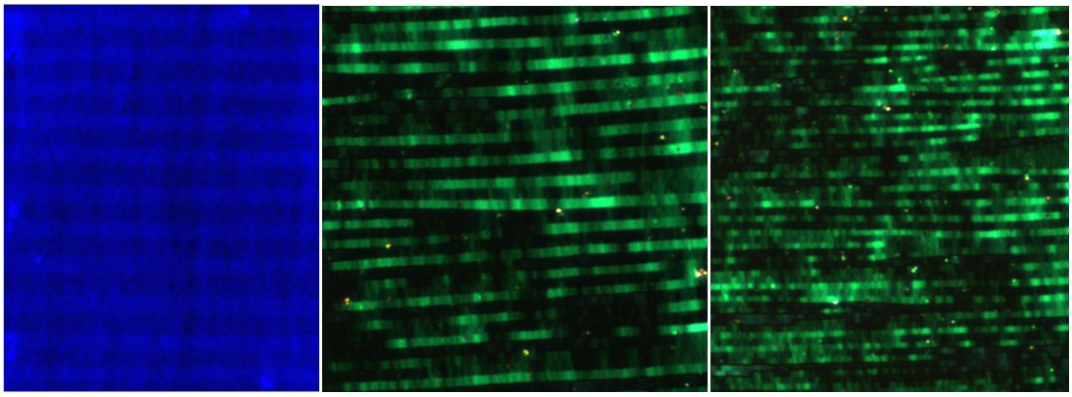

Figure 4. Domains with opposite switching are being shown. Left: microphotograph obtained using stroboscopic backlight, blue color is the color of the backlight LED. Middle and right: cell with asymmetric boundary conditions, the green color corresponds to 6.2μm birefringent sample thickness between the crossed polarizers. Polarizers are parallel to the image frame. Rubbing direction is set at a few degrees away from the vertical direction of the image. Applied voltage is square wave with an amplitude of 80 V. Frequency 7 kHz (middle) and 18 kHz (right).

Achiral symmetry of the system suggests the presence of the domains with opposite sign of switching as described in the previous section. These domains were observed experimentally and were reported[2]. For the small fields the domain configuration is rather random and is determined by the surface irregularities and the thermal history of the sample. In some cells a monodomain area can be as large as the microscope field of view, i.e. a few millimeters in diameter. Later we found that the application of the high fields and high frequencies produces a periodic striped pattern of these domains[3]. This is a completely different striped pattern from the one observed in planar cells without electric field. Low visibility and the field values close to the electrical breakdown make this pattern rather difficult to observe and analyze. So far these patterns were observed only in one mixture containing 65 wt. % of M2 and 35 wt. % of the monomer of M3. The temperature range is also rather narrow and is within 1°C from the N-N_{tb} phase transition. The following three experimental techniques have proven to be useful:

(i) Application of DC field or a bias for a short period after forming of the domain pattern with AC field. Note that a long-term application of DC field causes rapid degradation of the sample as well as the change in the domain pattern obtained under AC conditions.

(ii) stroboscopic illumination with ultra-bright light emitting diode (LED). This allow the image corresponding to only one polarity of the AC electric field to be observed/recorded by a camera, therefore the contrast between the right and

left domains is visible over a wide range of frequencies. (Figure 4, left). This technique is also well suited for automated experiments. Although the contrast of the obtained images is still rather low, it is enough to estimate the pattern periodicity using a Fourier transform image processing algorithm. The frequency dependence of the domain periodicity is shown in Figure 6.

(iii) Asymmetric boundary conditions of the cell. Middle and right sections of the Figure 4 show the domain pattern observed under ordinary white light illumination conditions. The contrast for the domains is provided by the absence of the alignment layer on one of the Indium Tin Oxide (ITO) electrodes, while the other carries a planar rubbed alignment layer (RN 1175, Nissan Chemicals, Japan). One can see a clear difference in the domain size, which is summarized in Figure 5 (left). Depending on the field and the waveform, the domains are decreasing with frequency.

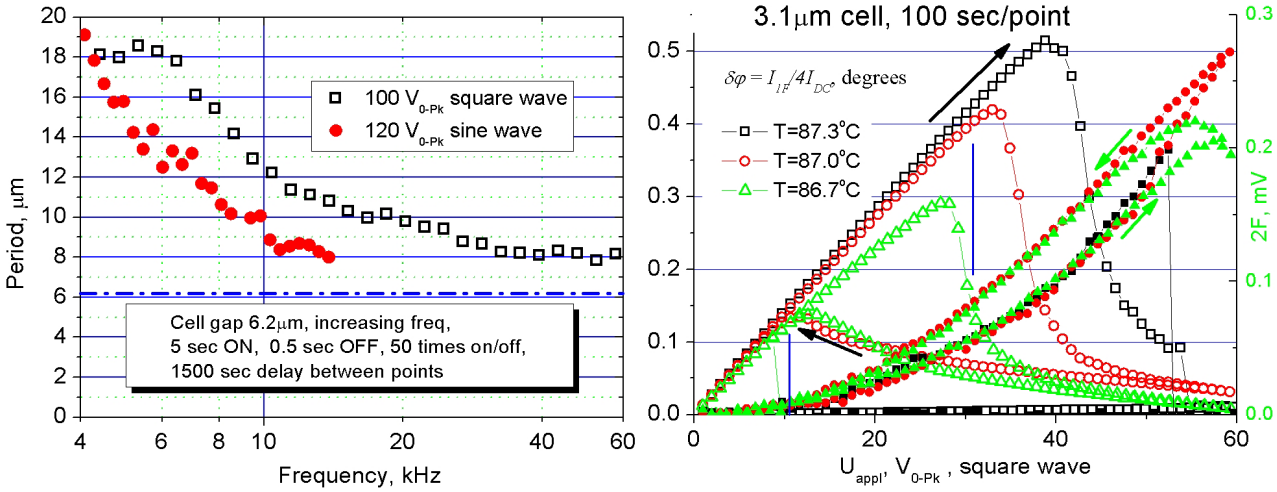

Figure 5. Right: Frequency dependence of the domain period obtained from images captured for different applied voltages at a temperature just below the Nu-Nx phase transition in the cell with asymmetric boundary conditions. Blue dash-dot line denotes the cell gap size of 6.2 micrometers. Left: Threshold behavior of the domains, 3.1 μm cell, 100 s/point, 7 kHz, square wave. Electric field is the abscissa voltage divided by the cell thickness. Blue dotted lines denote the field values of 3.5 V/μm and 10 V/μm. The increasing and decreasing of the electric field is specified by the black arrows near the corresponding data points. Solid symbols represent the second harmonic of the corresponding signals which is independent on the domain pattern.

In order to investigate the condition of appearance of the domain patterns, the set-up described in section 1.3 was used. A cell was fixed in a polarizing microscope with crossed polarizers at an angle of 22.5° between the polarizer and the rubbing direction. An AC voltage was applied to the cell and set-up was acquiring the transmittance of the light separating the components corresponding to DC, to the fundamental frequency (1f) and to the second harmonic (2f) of the applied signal. In the case when one single domain covers the entire field of view of the microscope, one can determine the in-plane deviation of the optical axis approximately as $\delta\varphi=I_{1f}/(4I_{DC})$. When a multidomain striped pattern appears, the first harmonic signals from the domains with opposite switching will cancel out and the first harmonic of the photodiode current detected by the lock-in amplified should drop to zero. Meanwhile the second harmonic, which is not sensitive to the direction of the optical axis deviation, should continue increasing. This is observed experimentally as shown on the right side of the Figure 5. One can see that the applied voltage should exceed a certain threshold in order for the domains to appear. The threshold is almost 10 V/μm for the temperature close to the N-N_{tb} phase transition and is increasing rapidly when cooling the sample. There is also a noticeable hysteresis: On decreasing the field, the monodomain level of the signal is restored at approximately 3.5 V/μm. The measurements were performed at a low speed, allowing for a settling time of 100 seconds at each voltage point. This is to negate the possible contribution to the hysteresis caused by the high viscosity of the N_{tb} phase.

2.5 Hysteresis in Freedericksz transition.

The hysteresis mentioned in the previous section is not the only case when hysteresis is observed in the N_{tb} phase. A noticeable hysteresis is also observed in the planar cells when the materials with positive dielectric anisotropy are subjected to the Freedericksz transition. Figure 6 clearly demonstrates the difference in the behavior between the nematic

(left) and the N_{tb} (right). The nematic phase in the dimer materials demonstrates classical curve of the transmittance as the function of the electric field. The cell also acts as a strong low-pass filter which eliminates most of the AC components of the signal. By contrast, the Freedericksz transition in the N_{tb} phase not only takes dramatically longer time (tens of seconds for N_{tb} vs. milliseconds in the N phase), it also shows clear hysteresis, which increases rapidly on cooling. Moreover, by observing the behavior of the AC components one can see that in contrast to the expected low-pass filter behavior, the applied square wave voltage is visible in the optical transmittance signal almost without distortion. This is one more illustration of the fast switching discussed in the section 2.3. The coexistence of such a dramatic viscosity increase with the appearance of the microsecond response is extremely intriguing. Moreover, there is definitely a room for theoretical exercise to explain the "latch" properties causing the hysteresis in the N_{tb} phase.

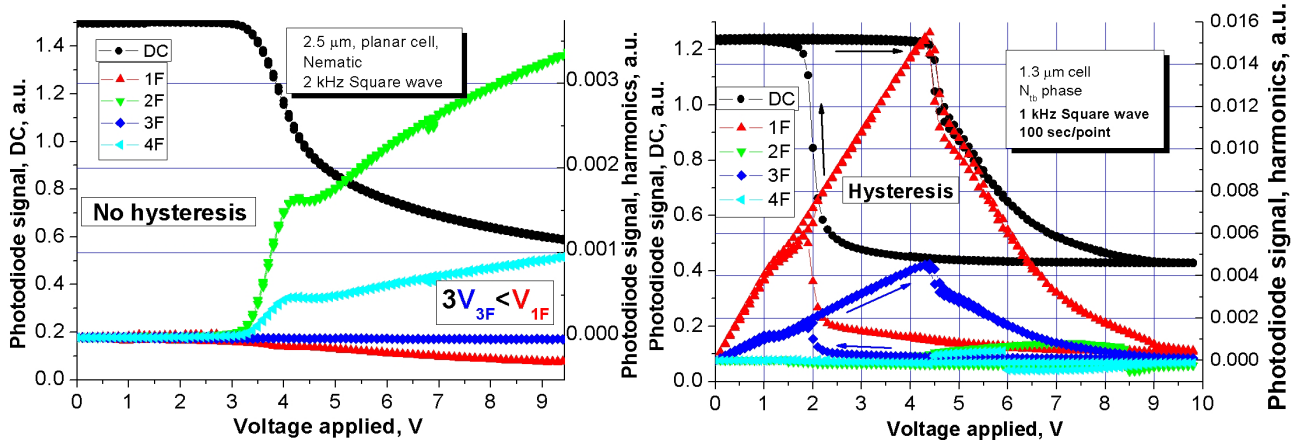

Figure 6. Freedericksz transition in planar samples of a dimer material with positive dielectric anisotropy. Conventional behavior of the nematic phase (left) and hysteresis in the N_{tb} phase (right). The data obtained using the set-up described in the section 2.2.

3. CONCLUSIONS.

While the recent studies give a number of fascinating answers for the questions related to the structure and properties of these novel materials, new questions arise and the properties of this phase remains one of the most intriguing topics in the field of liquid crystals. These include the explanations for a variety of the observed textures, of the electric field induced patterns of chiral domains and of the hysteresis phenomena. Further investigations of the properties of the fast response in the N_{tb} phase are required in order to increase the optical axis deviation angle. Hierarchy of the periodic structures found in the N_{tb} phase is not only extremely interesting from fundamental point of view, but it can also have potential for novel applications in micro- and nano-technology. The same applies to the opposite switching in the adjacent domains which suggests the presence of opposite chiral handedness. This can now be generated in a controllable manner using non-chiral molecules.

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